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Defect-effects on the photoluminescence of ZrO₂ bulk, film and nanocrystals

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ABSTRACT

The photoluminescence (PL) properties of ZrO_2 have been measured at different temperatures between 7 and 300 K, using various kinds of ZrO_2 specimens: bulk crystal melt-grown by a large solar furnace, thermally oxidized zirconium plate (ZrO_2 film crystal on Zr) and nanocrystals (surface area: 35-45 m²/g, diameter: 20-30 nm). The results clarify the deep and shallow energy level structures in the energy gap. Reversible UV-laser-light-induced spectral changes are observed for all of the specimens in different specimen-atmospheres (vacuum and O_2 gas). The results elucidate the defect-effects of the PL properties and the PL enhancement mechanism in ZrO_2 nanocrystals.

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1. Introduction

Zirconia (ZrO₂) is a well known metal oxide with useful mechanical, thermal, optical and electrical properties [1]. It crystallizes at room temperature in the monoclinic crystal structure. It has been reported that ZrO₂ film displays a Stokes-shifted intrinsic PL band and several extrinsic PL bands at about 4.3 and below 3.5 eV [2]. Also, it has been well known that intense, longlasting and white luminescence is excited by photons with lower energies than the energy gap ($E_g=5 \text{ eV}$), which is nothing other than in-gap excitation. Besides, since the PL intensity increases considerably with decreasing size, the nanosized particles are particularly interesting for the development of novel opto-electronic and sensor devices [3]. However, the detailed PL mechanism (optical excitation and its relaxation processes) for the in-gap photoexcitation of ZrO₂ is not fully elucidated. The first of the main reasons is that it is hard to grow ZrO₂ bulk crystal, which is an indispensable reference specimen for studying the nanocrystal nature. ZrO_2 has a high value of the melting point (> 2973 K) and therefore high-quality bulk crystal is hard to be grown without any flux. Fortunately, using a large solar furnace, we grew ZrO₂ crystal in air, without any crucible and any flux. The second is the difficulty in separating hafnium from zirconium. Usual ZrO₂ contains several percents of Hf atoms as impurity, which may create some shallow levels and other levels in the energy gap. In 2009, we reported the outline of the PL properties [4]. To obtain more correct conclusion, we have been carrying out more detailed experiments until today. In the experimental studies, a comparative study of PL properties of ZrO₂ has been carried out at different temperatures between 7 and 300 K, using bulk crystal

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melt-grown by a large solar furnace, thermally oxidized zirconium plate (ZrO_2 film crystal on Zr) and nanocrystals (surface area: $35-45 \text{ m}^2/\text{g}$, diameter: 20-30 nm) of ZrO_2 . Both the obtained time-resolved spectra and the excitation photon-energy dependence clarify the defect effects, especially, deep and shallow energy level structures in the forbidden gap.

2. Experimental

ZrO₂ bulk crystal was grown in air by melting a sintered disk with a solar furnace and by cooling gradually. X-ray diffraction (XRD) analysis of the grown crystal blocks proves that they are polycrystalline monoclinic ZrO₂. We named the bulk ZrO₂ crystal "solar furnace" for short, in Figs. 1-3. Commercial high-purity (Aldrich 99.99%) ZrO₂ powder was used as the purest ZrO₂ specimen. XRD analysis of the powder proves that the powder is monoclinic ZrO₂. We named the purest ZrO₂ powder "high purity powder" for short, in Figs. 1-3. Commercial ZrO₂ nanopowder (Aldrich, 20–30 nm in size) were used as ZrO₂ nanocrystal specimen. XRD analysis of the nanopowder proves that the powder is monoclinic ZrO₂. We named the ZrO₂ nanopowder "nanopowder" for short, in Figs. 1–3. Zirconium plate was oxidized at 1173 K in O2 gas stream for 7 h. The XRD analysis of the oxidized Zr plates shows that they are monoclinic ZrO₂ films. We named the oxidized Zr plate "oxidized surface" in short. Both the ZrO₂ powder, which is the starting material powder (20-30 nm in size) for the ZrO₂ bulk crystal, and ZrO₂ nanopowder (Aldrich, 25 nm in size) were used as ZrO₂ nanocrystal specimen.

The PL and photo-induced PL spectral change experiments were carried out with a continuous wave (CW) He–Cd laser line (wavelength λ =325 nm, photon energy hv=3.81 eV). The same He–Cd laser line excites luminescence. The emitted light is dispersed and detected using a grating spectrograph equipped





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Fig. 1. PL spectra of various ZrO_2 specimens at different temperatures (7 K \leq $T \leq$ 298 K).

with an image-intensified multichannel photodetection system. The time-resolved PL measurements were made using the same photodetection system to which two delay pulse generators were attached and a Nd³⁺–YAG laser (λ =355 nm, pulse width= 4–5 ns, repetition=10 Hz). In the measurements of excitation photon energy dependence, another Nd³⁺–YAG laser (λ =266 nm, pulse width=15 ns, repetition=10 Hz) was used. Vacuum of about 10⁻⁴ Pa and oxygen gas of about 0.1 MPa were used for the atmosphere around the specimen. Evacuation was carried out with an oil-free vacuum system consisting of a turbo-molecular pump and a mechanical diaphragm pump.

3. Results and discussion

We measured the PL spectra of various kinds of ZrO₂ specimens at different temperatures between 7 K and about 298 K. The results are shown in Fig. 1. The luminescence was excited by a CW 325 nm laser light. Since the energy gap of ZrO₂ is about 5 eV, the 325 nm photoexcitation corresponds to the in-gap excitation. The spectra are appropriately rescaled in this figure. Each rescaling factor is given in each figure, for example, x 1, x 2.4, etc. As shown



Fig. 2. Time-resolved PL spectra of various ZrO₂ specimens at 7 K.

in this figure, nanopowder exhibits the most intense luminescence and the high purity powder specimen does relatively weak luminescence. Except for nanopowder specimen, the spectral shapes and temperature dependences of three kinds of specimens indicate that their PL spectra consist of at least two kinds of luminescence centers, which emit luminescence around about 2.4 and about 2.5 eV. The high purity powder displays luminescence at photon energies higher than about 2.8 eV, while the contribution of the broad luminescence component around about 2.5 eV (which was prominently observed for the nanopowder, solar-furnace-grown crystal and oxidized Zr surface) is relatively small. It suggests that the PL band around 2.5 eV is extrinsic one. With increasing temperature, the PL intensity of ZrO₂ nanopowder increases slightly and then it reached a maximum of 36 K. Such temperature dependence is frequently observed for a broad band, which arises from several luminescence centers adjacent in energy. With further increasing temperature, the PL intensity is exponentially decreased up to about 298 K without changing the intensity peak energy. The activation energy (ΔE) for the PL intensity (I) decrease were calculated as 69.6 meV (=561 cm⁻¹), 81.3 meV ($=656 \text{ cm}^{-1}$), 6.8 meV ($=54.8 \text{ cm}^{-1}$) and 68.4 meV (=551 cm⁻¹) for the nanopowder, solar-furnace-grown crystal,



Fig. 3. Excitation wavelength dependence of PL spectra for various ZrO₂ specimens at room temperature.

high-purity powder and oxidized surface, respectively. Excepting for the high purity powder specimen, the ΔE of the white PL band is nearly close. These energies are the heights of an average potential barrier separating white luminescent states from the ground state.

Fig. 2 shows the time-resolved PL spectra of various ZrO₂ specimens at 7 K. The luminescence at energies higher than 2.7 eV disappears rapidly within 30 ns after excitation, and the luminescence at energies lower than 2.7 eV remains over 10 ms. However, the long-lasting luminescence band is not clear whether time resolved or not, but a faint spectral shift is seen. The shift is due to the time integration effect [5]. The PL decay curves of the longlasting luminescence were measured at 7 K and room temperature for all of the specimens. The results for the white PL band were examined with a power law and the multi-component-type exponential one. It is found that the decay curves are well fitted with a power law $(I \propto t^{-2})$ for all of the specimens at 7 K and room temperature. It indicates that the carriers photo-excited from defect-related in-gap states walk randomly via shallow traps and an accidental recombination with an ionized defect (and/or an impurity) creates a long-lasting PL.

Fig. 3 shows the excitation wavelength dependence of PL spectra of various ZrO_2 specimens at room temperature. As shown in Fig. 3(a), clear excitation-laser-wavelength-dependences on PL spectra are observed at photon energies higher than 2.6 eV for the nanopowder specimen. The wavelengths, 355 and 266 nm, correspond to 3.49 and 4.66 eV, respectively. These energies are close to those of the extrinsic PL bands observed by French et al. [1] for film specimen. The similar spectral structure is also observed for other specimens, as shown in Fig. 3(b)–(d). This indicates that there are many kinds of extrinsic luminescent levels in the energy gap, though the wavelength dependence of the light-penetration depth cannot be ignored. At the initial stage of photoexcitation, the laser light pulse is seen at twice the wavelength, 532 nm (=266 nm × 2=2.33 eV), of each spectrum, which is common to every grating monochromator.

Fig. 4(a) and (b) shows the reversible photo-induced spectral change of ZrO_2 nanopowder at room temperature in a vacuum and O_2 gas, respectively. The irradiation time is given by each curve. Fig. 4(c) shows the irradiation time dependence of the integrated PL intensity under vacuum (V) and oxygen (O_2) atmospheres. In the experiments, the 325 nm laser light irradiation in a vacuum induces the desorption of O_2 molecule creating various oxygen-deficient defect structures, while that in O_2 gas induces the adsorption of O_2 molecule at oxygen defect site with annihilating oxygen-deficient defect structures. Fig. 4(a) and (b) shows clearly how the PL spectrum changes with oxygen desorption and adsorption, for the first time. The PL band due to the oxygen desorption corresponds to about 2.3 eV. In the previous report [4], the PL intensity of ZrO_2 specimens is increased by 325 nm laser light irradiation in a vacuum. Very recently, we have measured



Fig. 4. Reversible photo-induced spectral transition of ZrO₂ nanopowder at room temperature.

the PL spectra in a wide laser fluence range and found the followings. Under intense excitation ($>1500 \text{ mW/cm}^2$), with increasing irradiation time in a vacuum, the PL intensity increases first and then it decreases. On the other hand, under weak excitation ($< 100 \text{ mW/cm}^2$), the PL intensity increases with increasing irradiation time in a vacuum. The main reason of the difference may be the phonon-assisted creation of non-radiative traps (namely, thermal-damage effects).

4. Concluding remarks

In the present study, the detailed experiments of the PL properties due to the in-gap photo-excitation were carried out for various kinds of ZrO₂ specimens. It is found that the bluish white PL of ZrO₂ consists of many luminescence components, which arise from extrinsic luminescence centers (various oxygendeficient defect structures, Hf-related defect structures and other impurities). Usually, ZrO₂ contain Hf, C and transition metal elements as impurities. Hf⁴⁺ ions may occupy randomly Zr⁴⁺ lattice point, creating shallow trap levels below the conduction band, while impurity transition elements ion and oxygen defects create deep donor levels in the energy gap. Anyway, electrons are excited from extrinsic in-gap states to the conduction band. The electrons move randomly throughout specimens, experiencing many trapping and releasing via shallow traps. Accidental recombination of the donor (which releases electron) and randomly walking electron produces a long-lifetime luminescence.

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